

1 **SENSOR FOR PERFORMING SURFACE ENHANCED RAMAN SPECTROSCOPY**
2 **AND METHOD FOR ACHIEVING SAME**
3

4 CROSS REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation-in-part of commonly assigned U.S. Patent Application
6 Serial No. 09/593,675, filed 14 June 2000, and entitled *A METAL AND GLASS STRUCTURE*
7 *FOR USE IN SURFACE ENHANCED RAMAN SPECTROSCOPY AND METHOD FOR*
8 *FABRICATING SAME*, and is a continuation-in-part of commonly assigned U.S. Patent
9 Application Serial No. 09/805,665, filed 13 March 2001, and entitled *SENSOR FOR*
10 *PERFORMING SURFACE ENHANCED RAMAN SPECTROSCOPY*.

11 BACKGROUND OF THE INVENTION

12 The present invention generally relates to the field of Raman spectroscopy, and more
13 particularly, to a sensor for detecting chemicals both in gas and liquid environments using
14 surface enhanced Raman spectroscopy in which any Raman scattering due to excitation of the
15 optical elements of the sensor are minimized..

16 Raman spectroscopy is an emission technique that involves inelastic scattering of
17 incident laser energy and results in spectral peaks that are frequency shifted from the incident
18 energy. The Raman bands arise from changes in polarizability in a molecule during vibration. As
19 a result, virtually all organic molecules display a characteristic Raman emission. Therefore, a
20 Raman sensor would not be limited to a specific class of molecules as is the case for the laser
21 induced fluorescence (LIF) sensor. Raman spectrometry allows the fingerprinting of species
22 present and is structurally specific. The inherently high resolution of Raman spectra often permits
23 the analysis of several components in a mixture simultaneously.

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1 The advent of inexpensive, portable Raman spectrometers has seen renewed interest in
2 the area of Raman spectrometry. This new generation of spectrometers employs fiber-optic
3 probes, holographic notch filters for rejection of the Rayleigh line, a single grating
4 monochromator, and a charge-coupled device (CCD) detector for multichannel detection. These
5 spectrometers contain a minimum of optical components as compared to conventional Raman
6 instrumentation resulting in high throughputs; and, once coupled to a laser and spectrometer,
7 optical-fiber probes require no further alignment.

8 Despite the advantages of Raman spectroscopy over other spectroscopic techniques and
9 the technological advances in the area of Raman spectrometry, Raman spectroscopy is,
10 inherently, an insensitive technique. To achieve detection limits in the low ppm range would
11 require either the use of a multiple pass cell or long acquisition times. In the 1970s, it was
12 discovered that Raman scattering from molecules adsorbed on such noble metals as silver,
13 copper, and gold can be enhanced by as much as 10^6 to 10^7 . This phenomenon, called surface
14 enhanced Raman spectroscopy (SERS), is still not understood despite intensive theoretical and
15 experimental research. It is believed that more than one mechanism is involved in the SERS
16 phenomenon. Initially, the SERS technique was used as a means to probe adsorption at metal
17 interfaces both in electrochemical and gas-phase environments. This technique has proven useful
18 in deducing the effects of interfacial structure and reactivity on the adsorption process.
19 However, the sensitivity of the technique as well as its exceptional spectral selectivity has made
20 SERS attractive for a broad range of analytical applications. SERS can be used for trace organic

1 analysis and as a detection method in gas chromatography, liquid chromatography, and thin layer
2 chromatography. Electrochemical SERS and SERS of chemically modified surfaces have been
3 used to detect aromatic compounds and chlorinated hydrocarbons, organic contaminants of
4 environmental concern, in the ppm concentration range.

5 There are many applications in which detection of particular chemical species or analytes
6 is desirable, as for example, hydrocarbons that may be present in ground water, toxic vapors in
7 industrial environments, explosives, metal ions, narcotics, toxic anions, and chemical warfare
8 agents.

9 However, Raman scattering as a result of excitation of the optical elements of the sensor
10 can obfuscate and/or interfere with detection of Raman scattering due to excitation of the species
11 of interest. Therefore, a need exists for a SERS sensor that minimizes or eliminates Raman
12 scattering due to excitation of the optical elements of the sensor.

13 SUMMARY OF THE INVENTION

14 The present invention provides a sensor for performing surface enhanced Raman
15 spectroscopy (SERS) that employs a computer for implementing algorithms that minimize, or
16 filter the influence of Raman scattering resulting from self-excitation of the optical elements of
17 the sensor on the spectral output of the sensor attributable to Raman scattering of a species of
18 interest.

19 A sensor performs surface enhanced Raman spectroscopy and employs a filter to
20 minimize the effects of Raman scattering to self-excitation of the optical elements of the sensor.

1 The sensor comprises: a) a sensor body having a throughbore; an optical energy source for
2 generating an optical excitation signal; b) a surface enhanced Raman scattering structure that is
3 mounted to the sensor body through which the optical excitation signal is directed for irradiating
4 an analyte, whereupon the analyte generates primary Raman emissions in response to being
5 irradiated by the optical excitation signal, and wherein the surface enhanced Raman scattering
6 structure generates secondary Raman emissions when irradiated by the optical excitation signal;
7 c) an optical detector for generating an output signal that represents the spectral characteristics of
8 the primary and secondary Raman emissions in response to receiving the primary and second
9 Raman emissions; and d) a processor for substantially filtering the secondary Raman emission
10 from the primary Raman emissions and for generating an output signal representing the analyte.

11 These and other advantages of the invention will become more apparent upon review of
12 the accompanying drawings and specification, including the claims.

13 BRIEF DESCRIPTION OF THE DRAWINGS

14 Figure 1 illustrates a first embodiment of a fiber optic sensor for performing surface
15 enhanced Raman spectroscopy that includes a SERS structure mounted to the window of the
16 sensor.

17 Figure 2 shows transmission curves for the bandpass filter of Figure 1 operating when the
18 excitation light signal has a wavelength of 852 nm.

19 Figure 3 shows transmission curves for the long pass filter of Figure 1 operating when the
20 excitation light signal has a wavelength of 852 nm.

1 Throughout the several view, like elements are referenced using like references.

2 DESCRIPTION OF THE PREFERRED EMBODIMENT

3 Referring to Figure 1, the present invention is directed to a sensor 10 for performing
4 surface enhanced Raman spectroscopy. The sensor 10 includes a sensor body 12 having a
5 throughbore 14 in which is positioned a fiber optic bundle 16 comprised of collection optical
6 fibers 18, excitation optical fiber 20, collimating lens 22, focusing lens 24, window 26, and a
7 Surface Enhanced Raman Spectroscopy (SERS) structure 28 that is described in commonly
8 assigned U.S. Patent Application Serial No. 09/593,675, filed 14 June 2000, and entitled *A*
9 *METAL AND GLASS STRUCTURE FOR USE IN SURFACE ENHANCED RAMAN*
10 *SPECTROSCOPY AND METHOD FOR FABRICATING SAME*, incorporated herein by
11 reference. Filter 30 is optically aligned and spliced to excitation optical fiber 20; and an optical
12 filter 32 is optically aligned and spliced to each of collection optical fibers 18. Bushing 36 is
13 threaded into sensor body 12 to secure the fiber optic bundle 16 within the bore 14 of the sensor
14 body 12. An O-ring 38 may be interposed between bushing 36 and sensor body 12 to provide a
15 watertight seal therebetween. Window 26 on which SERS structure 28 is bonded may be secured
16 to sensor body 12 using adhesives, not shown, or by mechanical means, such as flanges or
17 clamps.

18 In the operation of sensor 10, optical energy source 40 emits a light signal 42 that is
19 directed to propagate through excitation optical fiber 20. Optical energy source 40 may be
20 implemented as a krypton ion laser, near infrared (IR) diode laser, or Nd:YAG laser that

1 generates light signals having wavelengths in the range, by way of example, from 647 to 1064
2 nm. Optical filter 30 is a bandpass filter that removes Raman emissions that may be excited
3 within excitation optical fiber 20 by light signal 42. Light signal 42 is emitted from the polished
4 end of excitation optical fiber 20 and then is collimated by lens 22 and focused by lens 26 onto
5 the external surface 77 of the SERS structure 28 which is a SERS surface/liquid or SERS
6 surface/vapor interface when sensor 10 is being utilized. Next, focused and collimated light
7 signal 42 passes through window 26 and SERS structure 28 and is then emitted from sensor body
8 12 through the SERS structure 28 into the environment 44, which for example, may be a liquid
9 or gas in which an analyte of interest may be present.

10 To stabilize the SERS response of surface 77, as well as to protect the metal films of the
11 SERS structure 28 (described in detail in U.S. Patent Application Serial No. 09/593,675, filed 14
12 June 2000, and entitled *A METAL AND GLASS STRUCTURE FOR USE IN SURFACE*
13 *ENHANCED RAMAN SPECTROSCOPY AND METHOD FOR FABRICATING SAME*) the metal
14 films, made for example, of copper, silver, or gold, are coated. Thiols react with gold and silver
15 substrates to form a self-assembled monolayer (SAM) coating 79 on the surface 77 of SERS
16 structure 28. The SERS response of the thiol coating 79 may be used for calibration purposes.
17 The particular thiol coating 79 is selected to have an affinity for a specific class of analytes of
18 interest, where the analyte is the chemical that is desired to be detected by sensor 10. For
19 example, a thiol coating 79 of 1-propanethiol has an affinity for aromatic and chlorinated
20 solvents. A thiol coating 79 of dimethylaminoethanethiol hydrogen chloride has an affinity for

1 negative ions such as nitrate and sulfate. A thiol coating 79 of an 18-crown-6 thiol derivative has
2 an affinity for alkali metal ions such as sodium and potassium. Although particular examples of
3 thiol coatings 79 have been presented herein, it is to be understood that they are presented by way
4 of example only. The scope of the invention includes the use of other thiol coatings than those
5 specifically identified above, as required to suit the needs of a particular application.

6 If an analyte of interest is present in environment 44, then the interaction of light signal
7 42 and the analyte in the presence of SERS structure 28 stimulates the generation of primary
8 Raman emissions 48 that are transmitted through window 26, focusing lens 24, and collimating
9 lens 22, and then enter collection optical fibers 18. Primary Raman emissions 48 due to the
10 analyte(s) are directed by collection optical fibers 18 through long pass filters 32 which block the
11 Rayleigh line, thereby preventing self-excitation of Raman emissions in collection optical fibers
12 18. The primary Raman emissions 48 are directed to optical detector 50 which detects the
13 spectral components of signals 48. Secondary Raman emissions 49 are generally defined as
14 Raman emissions that are generated as a result of irradiation of optical elements in the sensor 10.
15 For example, secondary Raman emissions may be generated by irradiation of the thiol coating 79
16 of SERS structure 28 by light signal 42. Optical detector 50 generates signal 52 that represents
17 the primary Raman emissions 48, particularly, the spectral components of primary Raman signals
18 48. Light signals 49 may interfere, obfuscate, or otherwise make detection of the Raman
19 scattering resulting from stimulation of an analyte of interest in environment 44 more difficult.
20 Therefore, it is desirable to try to eliminate or mitigate the influence of light signals 49 so as to

1 more saliently distinguish signals 42.

2 Optical detector generally receives primary Raman light signals 48 and any secondary
3 Raman light signals 49 resulting from excitation of the thiol coatings 79 by light signal 42. In
4 response to receiving light signals 48 and 42, optical detector 50 generates an output signal 52
5 that represents the spectral characteristics of light signals 48 and 49. Processor 54 receives signal
6 52 and executes a computer program that substantially filters secondary Raman emissions
7 associated with light signal 49 from primary Raman emissions associated with light signal 48.
8 Processor 52 then generates an output signal 56 that represents an analyte of interest. One
9 technique by which the secondary Raman emissions that characterize light signal 49 may be
10 filtered from the primary Raman emissions that characterize light signal 48 is achieved whereby
11 processor 54 creates a sample file that represents the combined spectral characteristics of light
12 signals 48 and 49. Then, the computer program subtracts a reference file that represents the
13 spectral characteristics of signal 49 from the sample file to create a data file that substantially
14 represents only the spectral characteristics of primary Raman scattering signal 48. An example
15 of a commercial computer program suitable for use in conjunction with the present invention by
16 which representations, such as the reference file, of the spectral characteristics of one light signal
17 may be subtracted, or filtered from the representations, such as the sample file, of the spectral
18 characteristics of another light signal is known as *Spectra Calc*® by Galactic Industries, Inc.

19 Processor 54 may then employ additional software that uses the input file as an input to
20 an algorithm which generates a value or “score” that may be entered into a look-up table,

1 whereupon an output signal 56 is generated that represents the identity of one or more chemical
2 species associated with that particular score. The chemical species associated with that score
3 substantially have the spectral characteristics of the signal 48 when any of such chemical species
4 is excited by light signal 42. The algorithm may be derived using a commercially available
5 neural network program.

6 The reference file is created in a calibration process by exciting the thiol coating 79 on
7 surface 77 with excitation light signal 42 in the absence of any analyte that could generate
8 primary Raman scattering so that only light signals 49 are generated and directed to optical
9 detector 50 via optical fibers 32. In response to detecting light signals 49, optical detector 50
10 generates an output signal 52 that substantially represents only the spectral characteristics of light
11 signal 49. Processor 54 then creates and stores a reference file that represents the spectral
12 characteristics of light signal 49.

13 By way of example, collection optical fibers 18 and 20, and filters 30 and 32 are available
14 as a commercial package from Visionex, Inc., and may be selected for specific excitation
15 wavelengths. Figures 2 and 3 shows transmission curves for the bandpass filter 30 and long pass
16 filters 32, respectively, operating when excitation light signal 42 has a wavelength of 852 nm.
17 Figure 2 shows that the bandpass filter 30 has a very narrow bandpass centered about 850 nm and
18 a full width, half maximum of value of 7 nm. Figure 3 shows that the long pass filter 32 sharply
19 passes light having wavelengths of about 868 nm or higher, but sharply attenuates light having
20 shorter wavelengths than that.

1 Obviously, many modifications and variations of the present invention are possible in
2 light of the above teachings. It is therefore to be understood that within the scope of the
appended claims, the invention may be practiced otherwise than as specifically described.

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